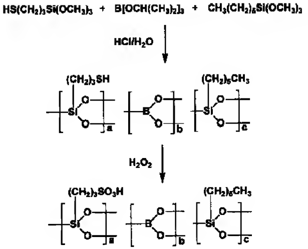
JAPANESE [JP,2002-184427,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS CORRECTION OR AMENDMENT

[Translation done.]

Drawing selection Drawing 1



[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the proton conductive substance which can be used more for the solid polymer electrolyte of a fuel cell, etc. at details about a proton conductive substance.
[0002]
[Description of the Prior Art]The fluoridation hydrocarbon system polymers electrolyte material which is a typical proton conductive polymer electrolyte membrane, At low humidity atmosphere or a not less than 100 ** elevated temperature, it has many faults, such as difficult, the permeability of fuel, such as that proton conductivity falls remarkably and methanol, i.e., control of a crossover, and a very expensive thing. The sulfonation thing (T. Kobayashi, M. Rikukawa, K.

Sanui, and N. Ogata, Solid State Ionics, Vol. 106, 219 (1998)) of usual hydrocarbon system polymer on the other hand, As an organic-inorganic hybrid type proton conductive material. On silicon, sulfonylbenzyl. The siloxane polymer which it has (I. Gautier, A. Denoyelle, J. Y. Sanchez, and C. Poinsignon, Electrochimica Acta, Vol. 37, 1615(1992)). And organic-inorganic hybrid polymer by which a siloxane and organic polymer were polymerization-ized by the urethane bond (I. Solid State) [Honma, S. Hirakawa, K. Yamada, and J. M. Bae,] Although Ionics, Vol.118, and 29 (1999) are reported, a synthetic method is complicated or there is a problem that proton conductivity is a little low. .On silicon, a methyl group. A tattered siloxane structure which it has. Although the organic-inorganic hybrid substance which it has is reported (G. D. Soraru, N.Dallabona, C. Gervais, and F. Babonneau, Chem. Mater. Vol. 11, 910 (1999)), It is not proton conductivity.

[0003]The fuel cell which is one of the applications of a proton conductive polymer is a cell using the energy produced from the electrochemical reaction of fuel and oxygen.

The structure which sandwiched the electrolyte membrane of proton conductivity between the fuel electrode and the oxidation electrode is known (JP,2000-277123,A, JP,2000-285933,A, JP,11-45733,A, JP,6-251780,A, etc.).

These operate this as a cell by constituting double layer pile ********** for the cell which generally stuck electrodes, such as platinum, on both sides of the electrolyte membrane about 50-200 micrometers thick, slushing another side to oxygen and hydrogen from one of these, and applying moderate back pressure at a moderate temperature. However, since the perfluorocarbon polymer (for example, Nafion (E. registered trademark of I.Dupont)) which generally has a sulfonic group as this electrolyte membrane is used like the gazette quoted here, it has the above-mentioned problem.

[0004]

[Problem(s) to be Solved by the Invention]It aims at providing an electrolyte material with high proton conductivity, and a simple manufacturing method for the same that this invention should solve the above-mentioned problem. In order to obtain high proton conductivity, a tattered siloxane skeleton is observed as a structure which promotes dissociative [of sulfonic acid] in this invention, As a result of inquiring about preparation of the tattered siloxane polymer by a hydrolysis condensation method with an easy

manufacturing method, and its sulfonation method, the organic-inorganic hybrid type proton conductor which has high proton conductivity was obtained.
[0005]
[Means for Solving the Problem]When a proton conductive substance has a boron content portion ($BO_{3/2}$), this invention persons, Dissociative [of sulfonic acid of a sulfonic group content portion ($Si(X-SO_3H)_xO_{(4-x)/2}$)] is promoted, it finds out that proton conductivity improves as a result, and this invention is completed. Namely, a proton conductive substance by which the purpose of this invention is expressed with following formula $(SiR^1{}_xO_{(4-x)/2})_a(BO_{3/2})_b(SiR^2{}_yO_{(4-y)/2})_c$ (among a formula) R^1 expresses -X-SO_3H (a carbon number expresses a hydrocarbon group of bivalence of 2-18 X among a formula.), A carbon number expresses a hydrocarbon group of monovalence of 1-18, more greatly than 0, x receives two or less, y receives more than [0 or less / 2], a and b receive a+b, R^2 is not less than 10% of 90% or less, respectively, and c is 0% or more of 80% or less to a +b+c. It is providing. This proton conductive substance can aim at improvement in performance by doping phosphoric acid. Another purpose of this invention is to provide a proton conductive substance which comprises stable polymers on these proton conductive substances and acid conditions. Another purpose of this invention is to provide a film whose thickness which comprises this proton conductive substance is 10-500 micrometers, and a fuel cell constituted by pinching this film between a fuel electrode and an oxidant electrode.
[0006]
[Embodiment of the Invention]The proton conductive substance (or organic-inorganic hybrid type proton conductor) of this invention, It has a tattered siloxane structure and a sulfonic group, and is expressed with following formula $(SiR^1{}_xO_{(4-x)/2})_a(BO_{3/2})_b(SiR^2{}_yO_{(4-y)/2})_c$. The portion which is the portion, portion, and optional component which are these essential ingredients $(SiR^1{}_xO_{(4-x)/2})$ $(SiR^2{}_yO_{(4-y)/2})$ does not need to constitute a block in order of the formula concerned, It may distribute at random and polymer may be constituted. That is, an upper type only shows a constituent and its quantitative ratio. In order to raise proton conductivity more, it thinks it more desirable for a boron content portion ($BO_{3/2}$) and a sulfonic group content

portion ($SiR^1{}_xO_{(4-x)/2}$) to approach more, and to constitute polymer.

[0007]R^1 of an upper type expresses $-X-SO_3H$ -- X -- a carbon number -- 2-18 -- the hydrocarbon group of the bivalence of 2-8 is expressed preferably, and if it is a hydrocarbon group of bivalence, there will be no other restrictions in particular. R^2 -- a carbon number -- 1-18 -- desirable -- 1-8 -- the hydrocarbon group of the monovalence of 2-6 is expressed more preferably, and if it is a hydrocarbon group of monovalence, there will be no other restrictions in particular. That is, X and R^2 may be a straight chain or branching, or may have an unsaturated bond, and may have an aromatic ring or alicycle. What is necessary is to become advantageous, when the compatibility at the time of mixing with polymers will increase for example, and it creates a film etc. if these carbon numbers become large, but just to choose it suitably for the purpose on the other hand, since proton conductivity will fall.

[0008]x is 1.1 or less [0.1 or more] more preferably 1.5 or less [0.01 or more] two or less more greatly than zero, and y is 1.1 or less [0.1 or more] more preferably 1.5 or less [0.01 or more] more than [0 or less / 2]. As for a and b, not less than 10% 90% or less each is not less than 40% of 60% or less more preferably not less than 30% of 70% or less to a+b. c is not less than 10% of 60% or less, and not less than 20% of 50% or less preferably 0% or more of 80% or less to a+b +c. As for these figures, it is preferred 0.1-20-mm equivalent weight /g, and that the sulfonic group in a proton conductive substance is suitably chosen so that it may be especially set to 1-5-mm equivalent weight / g. The proton conductive substance of this invention can raise the proton conductivity in an elevated temperature (about 100- about 180 **, especially about 100- about 150 **) by doping phosphoric acid. The doped quantity of desirable phosphoric acid is 0.1 to 50 millimol /g, especially one to 10 millimol /g to a proton conductive substance.

[0009]There is no restriction in particular about the process of the proton conductive substance of this invention, and it may create by a publicly known method. The example of the process is shown in drawing 1 (reaction mechanism 1) and drawing 2 (reaction mechanism 2).The compound shown in these figures is only a mere example, and this invention is not limited to these. The tattered siloxane polymer which has a sulfonic group is made to generate by making a polymer

generate and oxidizing a thiol group in the reaction mechanism 1 by carrying out the hydrolysis reaction of the alkoxysilane derivative and the ester of boric acid which have a thiol group. The tattered siloxane polymer which has a sulfonic group is made to generate by making a polymer generate and sulfonating a hydrocarbon group in the reaction mechanism 2 by carrying out the hydrolysis reaction of the alkoxysilane derivative and the ester of boric acid which have a hydrocarbon group. Namely, although the proton conductive substance of this invention can be manufactured simple by sulfonating following hydrolysis with an alkoxysilane derivative and the ester of boric acid, and a condensation reaction, Higher proton conductivity can be obtained by adopting a suitable reaction condition, as shown by the below-mentioned example. That is, in the reaction mechanism 1, as for the temperature at the time of oxidation reaction, 90 ** or less is preferred, and it is especially preferred. [of 70**5 **]

[0010]The blend system which made suitable polymers distribute the proton conductor of this invention can form a good film. as these polymers, degradation of stability, i.e., decomposition etc., is not caused under acid conditions -- if it kicks, other characteristics in particular will not be asked. A thermoplastic polymer may be sufficient as these polymers, they may be thermosetting polymers, and contain an organic high polymer and an inorganic polymer. For example, it is mentioned as that for which addition condensation system polymer, such as polystyrene and polyolefine, etc. were suitable, and a part of polycondensation system polymer has an unstable thing on acid conditions. Polyethylene oxide, styrene isoprene styrene block copolymer, polyvinylidene fluoride, silicon resin, etc. which are polystyrene sulfonate, bridging polystyrene sulfonate, or an aprotic conductive polymer as desirable polymers are mentioned. These polymers function as a structural material. What is necessary is just to choose them suitably with polymers suitable for the manufacture, if these polymers create the purpose, for example, a film. The proton conductor concerned may be mixed by a publicly known method to these polymer, and it may be made to polymerize after making a monomer distribute the proton conductor concerned.

[0011]The perfluorocarbon polymer (for example, Nafion) which is a proton conductive polymer and which has a sulfonic group may be used as a structural material. By mixing the proton conductive substance of this invention to

this perfluorocarbon polymer, it also becomes possible to become possible to raise proton conductivity further, therefore to reduce the amount of the expensive perfluorocarbon polymer used. Although the one where the content is higher generally has high proton conductivity, it is better for the content of the proton conductive substance of this invention in polymers to increase the rate of polymer, when it is going to receive film strength although it is dependent on the kind of polymers to be used. On the balance, 50 to 90% is preferred. When using the polymer which has a sulfonic group, 50% may be sufficient, and in the polymer which does not have a sulfonic group, 70 to 90% is good. It is also possible to introduce the bridged structure according to the demand of methanol crossover control, dimensional stability, etc.

[0012]Since the proton conductive substance of this invention has the outstanding proton conductivity, it can be used as an electrolyte membrane of a fuel cell. Constituting this film from the proton conductive substance and polymers of this invention as mentioned above, 10-500 micrometers of that thickness is usually 50-200 micrometers preferably. It can be made to function as a cell by constituting double layer pile ********** for the cell which stuck a fuel electrode and oxidation electrodes, such as platinum, on both sides of this film if needed, slushing fuel, such as another side to oxygen and hydrogen, from one of these, and applying moderate back pressure at a moderate temperature.

[0013]

[Example]Hereafter, although an example illustrates this invention, these are not what meant restricting this invention. Proton conductivity was measured by AC impedance method. The sample was created by heating tattered siloxane polymer at 100 ** for 1 hour, and was controlled by the spacer area ^{2} of 1.0x1.0 cm, and in the shape of [0.4 mm-thick] a square. The platinum board was used for the electrode. The schematic diagram of the device used for measurement is shown in drawing 3. 10-mV exchange was impressed to this, frequency was changed to 8 MHz - 0.0001 Hz, and it asked by carrying out the curve fit of the bulk resistor (R_b) using an equivalent circuit from the obtained Cole Cole plot. Ionic conductivity sigma (S/cm) As shown in a following formula, inter electrode distance d (cm) was computed by having broken it by the membranous cross-section area S (cm^2) and the product of resistance (S^{-1} (=omega)).

sigma = d/R_bS proton conductivity is so preferred that a numerical value is large, The proton conductivity of the perfluorocarbon polymer which has the usual sulfonic group is a 0.1 S/cm grade, and when using as a fuel cell, it is made preferred [the proton conductivity more than 0.1 S/cm].

[0014]The tattered siloxane electrolyte was created according to the reaction mechanism 1 shown in example 1 drawing 1.4.96 g (25.3 millimol) of 3-mercapto triethoxysilane, 4.77 g (25.3 millimol) of boric acid triisopropyl, and 10.3 g (49.9 millimol) of n-hexyl trimethoxysilane were dissolved into 100 ml of methanol. After adding the 0.04N HCl solution 3.59g (199 millimol) to the solution and making it stir at a room temperature for 24 hours, it stirred at 60 ** for 48 hours, and heating flowing back was performed further for 5 hours. When decompression removal of the solvent is carried out at a room temperature and reduced pressure drying was carried out at 90 more ** for 24 hours, transparent soft solid polymer was obtained (yield of 10.4g). 5 ml of H_2O_2 solutions were added to the flask containing 1.04 g of prepared polymer 30%, and it stirred at 70 ** (oxidation reaction temperature) for 1 hour. Decompression removal of the solvent was carried out after the end of stirring, and reduced pressure drying was further carried out at the room temperature for 24 hours. This output is called "the sample 70." The output which made oxidation reaction temperature 90 **, repeated the same operation, and was acquired is called "the sample 90." The obtained polymer was powder. In order to remove the sulfuric acid which generated a part of polymer furthermore obtained in the middle of oxidation, ultrasonic cleaning and filtration were performed 6 times by diethylether, and the tattered siloxane electrolyte was obtained. The yield and yield of a sample before and behind washing are shown in Table 1. In below-mentioned drawing 4 and 5, a washing sample shows the sample after washing and a sample shows the sample before washing.

[0015]

[Table 1]

サンプル名	サンプル 90	サンプル 70
反応温度(℃)	90	70
スルホン化に用いたサンプル量 (g)	1.04	0.615
スルホン化したサンプルの収率(g, %)	1.11, 90.9	0.63, 92.6
洗浄を行ったサンプル量(g)	0.300	0.366
洗浄を行ったサンプルの収率(g, %)	0.252, 84.0	0.323, 88.3

[0016]Although the tattered siloxane electrolyte which does

not contain a hexyl group was obtained by having used 3-mercapto triethoxysilane and boric acid triisopropyl as the starting material and the proton conductivity of the 10 $^{-1}$Scm^{-1} order was shown under high humidity, When it was going to blend with polymers and was going to generate the film, film formation nature was low, and there was deliquescence further. About the sample 90 and the sample 70, the proton conductivity sigma before and behind washing is compared, the relation between the relative humidity in 25 ** and proton conductivity is shown in drawing 4, and the temperature dependence of the proton conductivity in 95% of relative humidity is shown in drawing 5. In order that a thiol group may not stop at the oxidation to sulfonic acid but may oxidize even to sulfuric acid in part, if it oxidizes at 90 ** as shown in these figures, when washing removed sulfuric acid, the remarkable decline in proton conductivity was observed. However, about the sample which oxidized at 70 **, proton conductivity did not carry out a deer fall only by washing. That is, it is clear that oxidation reaction temperature's 70 ** is suitable. It was shown that the proton conductivity of the proton conductive substance of this invention is quite high.
[0017]4.91 g (25 millimol) of example 23-mercapto triethoxysilane, 4.73 g (25.1 millimol) of boric acid TORIISO pro yls, and 10.4 g (50.5 millimol) of n-hexyl trimethoxysilane were dissolved into 50 ml of 2-propanol.0.04N HCl solution, 0.25 g of tetraethylammonium tetrafluoroborate, and (1.15 millimol) 100 ml (50 millimol) of phosphoric acid (0.5 mol/(l.)) were added to the solution, and it was made to stir at a room temperature for 24 hours. Decompression removal of the solvent was carried out at the room temperature, and heat-treatment was performed at 140 ** for 2 hours. Reduced pressure drying was carried out at 90 ** after heat-treatment for 24 hours. After the earthenware mortar ground the obtained polymer powdered, it moved to the flask, 50 ml of H_2O_2 solutions were added 30%, and it stirred at 70 ** for 1 hour. Decompression removal of the solvent was carried out after the end of stirring, reduced pressure drying was further carried out at the room temperature for 24 hours, and the tattered siloxane electrolyte of the white powder which doped phosphoric acid was obtained. The temperature dependence of the proton conductivity in the inside of the air is shown in drawing 6. As for the decline in proton conductivity, more than 100 ** (1000/T= about 2.68) was small, and it has attained an

elevated temperature and high proton conductivity by a phosphoric acid dope.

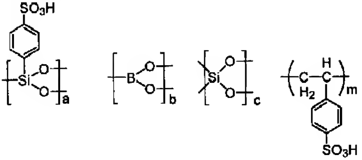
[0018]According to the reaction mechanism 2 shown in example 3 drawing 2, the tattered siloxane polymer which has a sulfonation phenyl group on silicon was compounded.6.29 g (31.7 millimol) of trimethoxy phenylsilane, 5.87 g of boric acid triisopropyl, and (31.2 millimol) water (0.1N HCl) 1.92 g (96 millimol) was put into a 30-ml flask. 100 ml of acetonitrile was added as a solvent, and it stirred at the room temperature for 5 hours. Next, temperature was raised to 60 **, and it stirred for 65 hours, and flowed back at 85 more ** for 3 hours. The solvent was removed by 80 ** and desiccation of 24 hours in the vacuum, and tattered siloxane polymer was obtained. Compound tattered siloxane polymer was broken and 0.202 g of broken polymer was moved to a 10-ml two-lot flask, and it melted in 3 ml of dichloromethane, carrying out the flow of the N_2. And 0.1 ml of chlorosulfuric acid ($ClSO_3H$) was added and sulfonated slowly. The mixture was stirred at 0 ** for 3 hours, after distilling off a solvent, in order to flush unreacted sulfuric acid, the ultrasonic cleaner was used several times and diethylether washed. And it dried in the room temperature and the vacuum for 24 hours, and the sulfonated tattered siloxane electrolyte was obtained. Although not shown for details, the tattered siloxane electrolyte which has the same character was obtained by repeating the operation same as a raw material for a trimethoxy benzylsilane instead of trimethoxy phenylsilane.

[0019]6.27 g (31.6 millimol) of example 4 trimethoxy phenylsilane, 5.91 g (31.4 millimol) of boric acid triisopropyl, and 1.287 g (12.36 millimol) of styrene were put into a 300-ml flask, and 100 ml of acetonitrile was used for the solvent. Water (0.1N HCl) 2.51 g (139.4 millimol) and recrystallized azobisuisobutironitoriru 0.64g (3.90 millimol) were added, and it stirred at the room temperature for 5 hours. And temperature was raised to 60 **, it stirred for one week, and flowing back was performed for further 3 hours. The solvent was removed by 80 ** and desiccation of 24 hours in the vacuum, and uniform yellow solid polymer was obtained. It is thought that this solid polymer constitutes the mutual invasion network structure (IPN) of tattered siloxane polymer and polystyrene. Compound polymer was broken and 0.501 g of broken polymer was moved to a 10-ml two-lot flask, and it melted in 5 ml of dichloromethane, passing nitrogen gas. And 0.3 ml of chlorosulfuric acid ($ClSO_3H$) was added and

sulfonated slowly. The mixture was stirred at 0 ** for 3 hours, after distilling off a solvent, in order to flush unreacted sulfuric acid, the ultrasonic cleaner was used several times and diethylether washed. It dried in the room temperature and the vacuum for 24 hours, and hybrid polymer of a tattered siloxane electrolyte and polystyrene was obtained. The hybrid system of the sample which changed the ratio of styrene, the polystyrene sulfonate which added and carried out the bridging of the divinylbenzene (DVB), and tattered SHITOKISAN, and the system to which the bridging of the tattered siloxane was carried out by adding a tetraethoxysilane (TEOS) were also prepared.

[0020]The proton conductivity of the tattered siloxane electrolyte obtained in Examples 3 and 4 is shown in drawing 7. In drawing 7, "A" with the structural formula of ** 1 The hybrid system electrolyte of polystyrene sulfonate of a:b:c:m=1:1:0:4, and a tattered siloxane, "B" with the structural formula of ** 1 The hybrid system electrolyte of polystyrene sulfonate of a:b:c:m=1:1:0:0, and a tattered siloxane, "C" with the structural formula of ** 1 The hybrid system electrolyte of polystyrene sulfonate of a:b:c:m=1:1:0:1, and a tattered siloxane, The electrolyte which carried out the bridging of "DVB-10" by divinylbenzene (DVB) 10% of a:b:c:m=1:1:0:4 with the structural formula of ** 1, And "TEOS-0.2" expresses with tetraethoxysilane (TEOS) 20% of a:b:c:m=1:1:0.2:4 the electrolyte material which carried out the bridging with the structural formula of ** 1.

[Formula 1]



Drawing 7 shows that the proton conductivity in which the proton conductive substance of this invention is quite expensive is shown.

[0021]The electrolyte which blended 10% of the weight of styrene isoprene styrene block copolymer (SIS) to a tattered siloxane electrolyte output which does not contain the hexyl group prepared in example 5 Example 1 was prepared by the following method.SIS 0.036g was melted until it became a solution uniform in a toluene solvent (1 ml). The toluene

solution of SIS was added to the tattered siloxane electrolyte 0.324g, stirring on an earthenware mortar. When it moves to a flask and reduced pressure drying was carried out at the room temperature for 24 hours, the hard solid blend electrolyte was obtained by the shape of rubber. The proton conductivity of the blend system of a tattered siloxane electrolyte and SIS is shown in drawing 8. It turns out that quite high proton conductivity is shown under a high humidity condition. Although not shown for details, the blend system electrolyte of these and a tattered siloxane electrolyte was obtained by using polymers, such as polyethylene oxide, polypropylene oxide, Nafion, or vinylidene fluoride, instead of SIS, and repeating the same operation. These showed the similarly outstanding proton conductivity.

[0022]

[Effect of the Invention]Dissociation of a sulfonic group is promoted by introduction of Lewes acidity boron, and the proton conductive substance of this invention has high proton conductivity by it. The proton conductivity in an elevated temperature (about 100- about 180 **, especially about 100- about 150 **) can be raised by doping phosphoric acid. The proton conductive substance of this invention is compoundable simple from organic silicon alkoxide and the ester of boric acid. Furthermore, when the proton conductive substance of this invention chooses suitably the hydrocarbon group which could prepare other polymers and blend systems easily and introduced them into the proton conductive substance, the compatibility with polymers improves and membranous generation becomes easy. Bridged-structure introduction is also possible. The generated film can be used as an electrolyte membrane for fuel cells.

[Translation done.]